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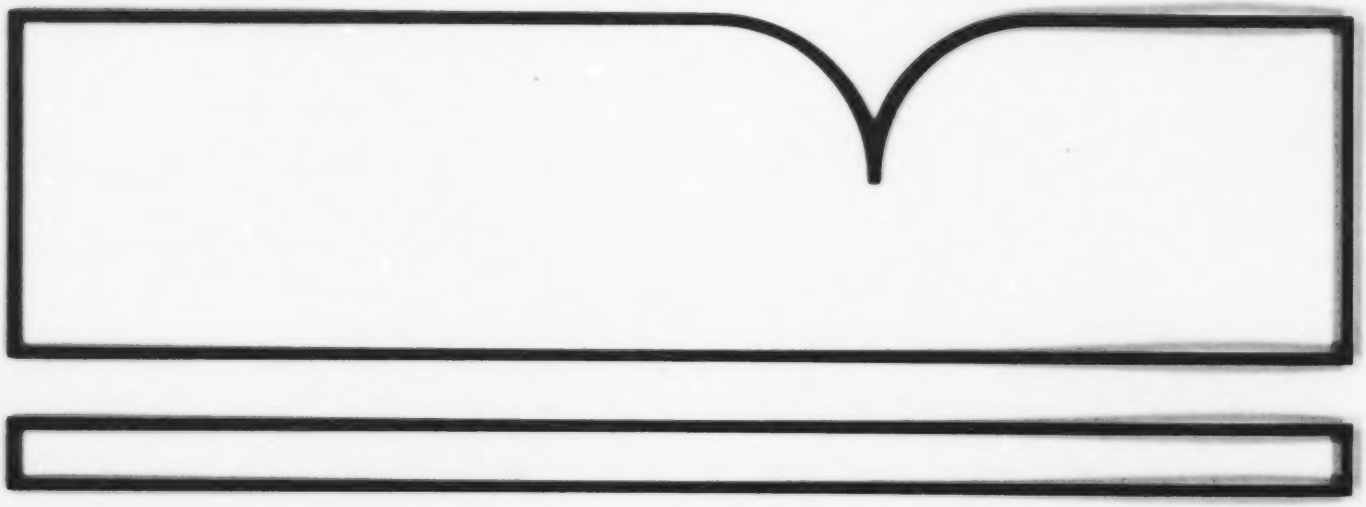

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16. ABSTRACT

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JOURNAL ARTICLE

# EMPIRICAL MODELS FOR LAKE ACIDIFICATION IN THE UPPER GREAT LAKES REGION

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ABSTRACT. A large data base on inland lakes in the Upper Great Lakes Region (UGLR) was used to evaluate assumptions and relationships of empirical acidification models. Improved methods to calculate background alkalinity and background $SO_4^{2-}$ are reported; $SO_4^{2-}$ enrichment factors indicate that terrestrial $SO_4^{2-}$ sources and watershed or lake sinks must be considered for site-specific backgound $SO_4^{2-}$ estimates. Significant relationships were found between lake acidification estimated as change in $SO_4^{2-}$ and precipitation acidity but not between changes in lake alkalinity and precipitation acidity in this lightly impacted region.

## 1. INTRODUCTION

Several empirical models have been developed to predict lake acidification based on titration and ion balance (electroneutrality) concepts. The simplest description of long-term lake acidification is the titration of alkalinity by atmospheric inputs of $H_2SO_4$. Thus acidification can be measured in two ways: loss of alkalinity ($\Delta$Alk) and increase in sulfate($\Delta SO_4$). Quantification of these terms requires knowledge of the original lake conditions, i.e. alkalinity and sulfate concentrations prior to enhanced deposition of sulfate from anthropogenic sources.

Criticisms of existing models stem from assumptions used to estimate these parameters. Original alkalinity ($Alk^o$) was estimated by Henriksen (1980) as a function of Ca or (Ca+Mg). This implies that weathering of other base cations contributes negligibly to Alk production or is constant among all watersheds. Original (background) sulfate ($SO_4^o$) has been ignored or assumed constant in a region (e.g. Henriksen, 1980). This assumes terrestrial S sources and site-specific $SO_4^{2-}$ sinks (e.g. biological reduction and soil adsorption) are unimportant.

We used a large data base of chemistry, hydrologic, and land-use data for lakes across the UGLR in conjunction with a precipitation chemistry data base to evaluate these assumptions. This paper describes improved methods to calculate lake-specific estimates of $Alk^o$ and $SO_4^o$ by use of a complete electroneutrality statement. The importance of local sources and sinks for sulfate in lakes of this region is demonstrated; preliminary atmospheric loading-lake response relationships are summarized.

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## 2. THE UPPER GREAT LAKES DATA BASE

The lake chemistry data base includes 1547 lakes in Minnesota, northern Wisconsin, and Upper Michigan. Data were obtained from the U.S. EPA, Minnesota Pollution Control Association (MPCA), and U.S. Forest Service (USFS). EPA data represent averages for 837 lakes sampled across the region from 1978-1983. Parameters include hydrologic type (Eilers et al.,1983), pH, alkalinity, color, major ions and nutrients. The MPCA and USFS data are averages for 710 Minnesota lakes sampled during the same time period. Parameters include pH, alkalinity, color, and major ions. Annual average wet deposition data for 21 sites across the region were obtained from NADP, MPCA, and Ontario monitoring networks. Variables include pH, $SO_4^{2-}$, and $Cl^-$. Annual deposition and annual average concentration of precipitation components were interpolated for each lake (Pratt, 1985). Acidic components increase from west to east across the region; $H^+$ ranged from 6 to 49 $\mu eq\ L^{-1}$ and $SO_4^{2-}$ from 20 to 68 $\mu eq\ L^{-1}$.

Several criteria were used to select data for model evaluation and development (Table I). Data were inspected for consistency; lakes with reasonable ion balances ($0.80 < \sum+/\sum- < 1.50$) were included, but lakes with $Cl^- > 5\ mg\ L^{-1}$ (an indicator of cultural influence) were deleted. Frequency distributions by alkalinity and hydrologic class (Figure 1) illustrate regional distributions of acid-sensitive lakes and the relative importance of various water sources. According to Eilers et al. (1983), the most acid-sensitive lakes in the region are precipitation-dominated seepage lakes. Nearly 40% of the lakes in the data base are seepage lakes, and most of these are acid-sensitive ($Alk < 200\ \mu eq\ L^{-1}$). Overall, one-third of the lakes are acid-sensitive by this criterion.

To determine whether unmeasured organic anions explain the anion deficits found in most ion balances, we computed anion contributions from organic color for 511 lakes by the method of Oliver et al. (1983). Comparison between initial and corrected ion balances showed that organic anions were insignificant at color < 50 PCU (n = 414), but significant contributions were found at color > 50 PCU (n = 97). To maintain consistency with data used for previous models and minimize uncertainty in calculations, we selected lakes with $Alk < 500\ \mu eqL^{-1}$ and color < 50 PCU for model evaluation and development of loading-response relationships. This included 505 lakes with complete major ion data (Table II).

## 3. BACKGROUND SULFATE AND ORIGINAL ALKALINITY

Background sulfate in lakewater ($SO_4^\circ{}_l$) is naturally occurring sulfate from atmospheric or terrestrial sources. This parameter is needed to compute both $Alk^\circ$ and $\Delta SO_4$.. Our estimates were calculated from background precipitation estimates ($SO_4^\circ{}_p$) and evaporative concentration factors. A range for $SO_4^\circ{}_p$ was estimated as follows. $SO_4^\circ{}_p$ in remote areas was estimated to be 5 $\mu eq\ L^{-1}$ (Galloway, 1985). This probably is a global minimum value, and $SO_4^\circ{}_p$ in many terrestrial areas is likely influenced by natural S sources: volcanoes, S-bearing minerals, $H_2S$

Table I. Lake Selection Criteria ($N_{initial}$ = 1547)

| Criterion | $\sum+/\sum-$ | $Cl^-$ < 5.0 mg $L^{-1}$ | Color < 50 PCU | Alk < 500 μeq $L^{-1}$ | Incomplete ion analysis |
|---|---|---|---|---|---|
| N lakes remaining | 1509 | 1472 | 1155 | 705 | 505 |

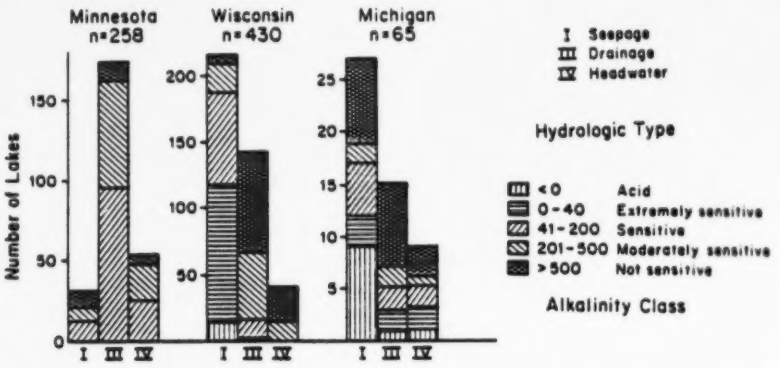


Figure 1. Alkalinity ranges for hydrologic classes. A majority of UGLR lakes with Alk < 200 μeq $L^{-1}$ are precipitation-dominated seepage lakes.

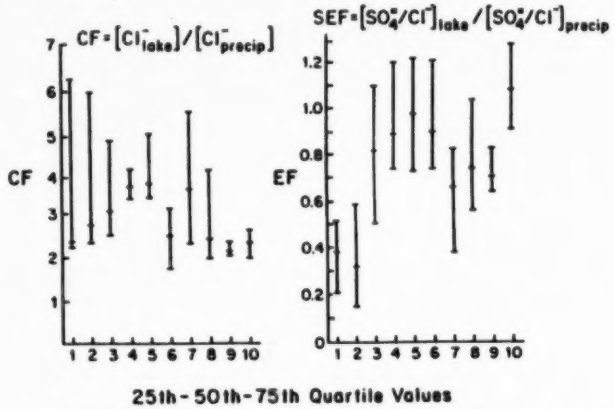


Figure 2. 25th, 50th and 75th quartile values of CF and SEF for counties across the UGLR (west to east). 1-5, Minnesota counties; 6-8, Wisconsin counties; 9-10, Michigan counties. CF range indicates that precipitation ions should be concentrated ca. 2-4X in lakes; EF range illustrates importance of watershed processes in determining lake $[SO_4^{2-}]$.

TABLE II. DESCRIPTIVE STATISTICS FOR UGLR LAKES USED IN ANALYSIS (N = 505)

| Parameter | | Mean | Std. Dev. | Max | Min |
|---|---|---|---|---|---|
| Alkalinity | $\mu eq\ L^{-1}$ | 163 | 134 | 500 | -38 |
| pH | | 6.67 | 0.64 | 9.00 | 4.44 |
| Conductance | $\mu S\ cm^{-1}$ | 30 | 14 | 71 | 9 |
| Color | PCU | 18 | 13 | 50 | 0 |
| $Cl^-$ | $\mu eq\ L^{-1}$ | 13 | 14 | 117 | 1 |
| $SO_4^{2-}$ | " | 81 | 30 | 189 | 1 |
| $Ca^{2+}$ | " | 142 | 90 | 485 | 25 |
| $Mg^{2+}$ | " | 74 | 48 | 297 | 21 |
| $Na^+$ | " | 32 | 19 | 121 | 1 |
| $K^+$ | " | 15 | 10 | 72 | 4 |
| $\sum^+/\sum^-$ | " | 263/261 | 143/139 | 704/702 | 64/60 |

emissions from wetlands, and sulfate-rich soils. Precipitation in the UGLR is influenced by all but the first source: prairie soils to the west are high in $CaSO_4$; wetlands are abundant in the region; localized sulfide mineral deposits occur, especially in NE Minnesota. Although we cannot quantify these sources from present data, it is reasonable to assume that $SO_4^{\circ}{}_p$ in the UGLR is above the global minimum. An upper bound for $SO_4^{\circ}{}_p$ can be obtained from an empirical model (Pratt, 1985) that relates pH and ion concentrations in precipitation. Background estimates calculated for the UGLR by this model are 23 to 29 $\mu eq\ L^{-1}$. Because recent data were used for these estimates, they likely are higher than historical levels. A reasonable range of $SO_4^{\circ}{}_p$ for the UGLR is 10 to 20 $\mu eq\ L^{-1}$ (between the global minimum and estimates from Pratt's model).

If we assume there are no local sources and that $SO_4^{2-}$ behaves conservatively, we can estimate $SO_4^{\circ}{}_l$ as the product of $SO_4^{\circ}{}_p$ and evaporative concentration. Assuming $Cl^-$ is conservative, we can estimate the latter from the ratio $CF = [Cl^-]_l/[Cl^-]_p$, which acts as a surrogate for hydrologic data. Atmospherically-derived $SO_4^{\circ}{}_l$ thus is: $SO_4^{\circ}{}_l = SO_4^{\circ}{}_p \times CF$. $Q_{25}$-$Q_{75}$, the first to third quartile range for CF (Figure 2a), is 2.3 to 4.4, and the median is 3.3; this implies that $SO_4^{\circ}{}_l$ should be ca. 2-4X higher than $SO_4^{\circ}{}_p$, or 20-80 $\mu eq\ L^{-1}$.

Regional variations in $SO_4^{\circ}{}_l$ result from variations in CF and from $SO_4^{2-}$ sources or losses in watersheds, the importance of which can be evaluated from $SO_4^{2-}$ enrichment factors (SEF): $([SO_4^{=}]/[Cl^-])_l/([SO_4^{=}]/[Cl^-])_p$. SEF > 1 indicates watershed sources; SEF = 1 indicates conservative behavior; and SEF < 1 indicates lake or watershed sinks. A bare majority of lakes in the UGLR exhibit nearly conservative behavior ($0.75 < EF < 1.25$) (Figure 2b). Estimates of $SO_4^{\circ}{}_l$ based on $SO_4^{\circ}{}_p$ and CF should be valid for these lakes. Some lakes, especially in NE Minnesota, have significant terrestrial sources; $SO_4^{2-}$ reduction or other sinks are important in nearly 40% of the lakes. Watershed sources or S can be estimated from a lake's SEF and present $[SO_4^{2-}]$, but because the influence of watershed processes on Alk and base cation levels in such lakes is uncertain, we did not use them to develop acidification relationships.

Existing models estimate $Alk^\circ$ from Ca or (Ca + Mg). This assumes contributions from Na and K are negigible or regionally constant (Kramer and Tessier, 1982). For UGLR lakes with Alk < 200 $\mu eq\ L^{-1}$, the average (Na + K) contribution to total cations ($\sum BC$) is 21%, $Q_{25}$-$Q_{75}$ is 16 to 23%, and the total range is 8 to 62%. Weathering of Na and K thus contributes varying but significant amounts of Alk to acid-sensitive lakes. Errors can be reduced by using all base cations to estimate $Alk^\circ$, which is best defined by the electroneutrality condition:

$$Alk^\circ = \sum BC^\circ - Cl^- - SO_4^\circ{}_l = \sum BC - \Delta\sum BC - Cl^- - SO_4^\circ{}_l \quad (1A)$$
$$= \sum BC - F\Delta\ SO_4 - Cl^- - SO_4^\circ{}_l \quad (1B)$$

Superscript $^\circ$ denotes background values; $Cl^-$ is the present value, (assumed constant); $\Delta\sum BC = F\Delta SO_4$ is the change in $\sum BC$ resulting from increased $SO_4^{2-}$ loading; F is the cation enhancement factor (e.g. Henriksen, 1980). We found no statistical evidence for a non-zero F in the UGLR. For the present, we assume F = 0. This may be reasonable for seepage lakes, which have little interaction with watersheds. Thus the equation, $Alk^\circ = \sum BC - Cl^- - SO_4^\circ{}_l$, provides lake-specific estimates of $Alk^\circ$, uses all available data and maintains the ion balance.

## 4. LAKE ACIDIFICATION AND LOADING-RESPONSE ESTIMATES

Lake acidification (estimated as change in alkalinity or sulfate) can be calculated from measured lake chemistry and estimated $SO_4^\circ{}_l$ and $Alk^\circ$: $\Delta Alk = Alk^\circ - Alk^m$, and $\Delta SO_4 = SO_4^m - SO_4^\circ{}_l$. Superscript m denotes present values. A 1:1 relationship is expected between $\Delta Alk$ and $\Delta SO_4$. The two terms are not independent, however, because $SO_4^\circ{}_l$ is common to both. Consequently, the relationship is a restatement of the electroneutrality condition. Regression analysis of the 505 lakes yielded the expected trend, with slope near 1 and intercept near 0 for the estimated range of $SO_4^\circ{}_p$: $\Delta Alk = 11.7 + 0.92\Delta SO_4$, $p < .0001$, (for $SO_4^\circ{}_p = 10\ \mu eq\ L^{-1}$); and $\Delta Alk = 8.4 + 1.01\Delta SO_4$, $p < 0.001$ (for $SO_4^\circ{}_p = 20\ \mu eq\ L^{-1}$).

Negative or very high $\Delta Alk$ and $\Delta SO_4$ were found for some lakes; as indicated by SEF values, these lakes have local sources or sinks of $SO_4^{2-}$ (Rogalla, 1986). In the latter case, estimates of $SO_4^\circ{}_l$ are too high, causing low or negative $\Delta Alk$ or $\Delta SO_4$. Conversely, $SO_4^\circ{}_l$ is underestimated for lakes with terrestrial sources of S, and $\Delta Alk$ and $\Delta SO_4$ are too high. For lakes with roughly conservative $SO_4^{2-}$ behavior (0.75 < EF < 1.25) and $SO_4^\circ{}_p = 10$ or 20 $\mu eq\ L^{-1}$, respective $Q_{25}$-$Q_{75}$ ranges for $\Delta Alk$ are 46 to 83 $\mu eq\ L^{-1}$ and 22 to 55 $\mu eq\ L^{-1}$; coresponding values for $\Delta SO_4$ are 42 to 61 $\mu eq\ L^{-1}$ and 16 to 36 $\mu eq\ L^{-1}$. $\Delta ALk$ and $\Delta SO_4$ estimates for these lakes should represent change by atmospheric inputs, and these were used develop loading-response relationships.

Relationships between precipitation acidity and acidification estimates were developed by regression analysis. Table III summarizes results for seepage and drainage lake subsets. The $\Delta SO_4$-$H^+_{prec}$ relationships are statistically significant and not different from each other. Intercepts

TABLE III. LOADING-RESPONSE RELATIONSHIPS FOR LAKES WITH EF ≈ 1.

| | | F | p | $R^2$ (%) |
|---|---|---|---|---|
| **Seepage Lakes (N=83)** | | | | |
| $\Delta SO_4(10)$* | = 22.3 + 1.61 $H^+_p$ | 13.7 | < 0.01 | 14.5 |
| $\Delta SO_4(20)$ | = -15.8 + 2.32 $H^+_p$ | 43.8 | < 0.01 | 35.1 |
| $\Delta Alk(10)$ | = 56.8 + 0.10 $H^+_p$ | < 1 | >> 0.10 | 0 |
| $\Delta Alk(20)$ | = 18.7 + 0.80 $H^+_p$ | 1.4 | > 0.10 | 1.7 |
| **Drainage Lakes (N=60)** | | | | |
| $\Delta SO_4(10)$ | = 24.2 + 1.78 $H^+_p$ | 11.4 | < 0.01 | 16.4 |
| $\Delta SO_4(20)$ | = -17.7 + 2.32 $H^+_p$ | 22.5 | < 0.01 | 28.0 |
| $\Delta Alk(10)$ | = 34.6 + 1.16 $H^+_p$ | < 1 | >> 0.10 | 0.6 |
| $\Delta Alk(20)$ | = 76.5 + 0.62 $H^+_p$ | 1.2 | >> 0.10 | 2.0 |

* Values in parentheses represent assumed $SO4^\circ_p$ in $\mu eq\ L^{-1}$.

for $SO_4^\circ_p$ = 10 $\mu eq\ L^{-1}$ are positive, while those for 20 $\mu eq\ L^{-1}$ are negative, which suggests that the true value of $SO_4^\circ_p$ is in this range. (An intercept of 0 would be expected for lakes at steady state with respect to atmospheric inputs.) The ΔAlk relationships are not statistically significant, probably because local (lake and watershed) processes that produce or consume Alk are sufficiently variable to mask regional relationships in this area of relatively low loading of atmospheric acidity.

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